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OTTAWA HULL K1A 0C9

(11) (C) **1,331,507**

(21) 502,324

(22) 1986/02/20

(45) 1994/08/23

(52) 31-63
C.L. CR. 150-26

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(51) INTL.CL.[5] C09K-005/04; G01M-003/20

(19)(CA) **CANADIAN PATENT** (12)

(54) Polyhalogenated Hydrocarbon Refrigerants and Refrigerant Oils Colored with Fluorescent Dyes and Method for their Use as Leak Detectors

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(30) (US) U.S.A. 704,666 1985/02/25

(57) 12 Claims

NO DRAWING

502324

P-302

POLYHALOGENATED HYDROCARBON REFRIGERANTS AND REFRIGERANT OILS COLORED WITH FLUORESCENT DYES AND METHOD FOR THEIR USE AS LEAK DETECTORS

ABSTRACT

A leak detectable refrigeration composition including a polyhalogenated hydrocarbon refrigerant, a refrigeration oil, or a mixture of the two having a fluorescent dye dissolved therein, is prepared for use in refrigeration systems in automobile air conditioning systems, commercial refrigeration systems, and the like. Upon exposure to ultraviolet light, there is sufficient fluoresence by the refrigeration liquid to allow one to visually detect a leak in the system due to the presence of the dye at the source of the leak. Small leaks which were previously nondetectable with dye coloring systems detectable in normal light may now be detected due to the greater visibility of the fluorescent dye under an ultraviolet light.

POLYHALOGENATED HYDROCARBON REFRIGERANTS AND REFRIGERANT OILS COLORED WITH FLUORESCENT DYES AND METHOD FOR THEIR USE AS LEAK DETECTORS

TECHNICAL FIELD

This invention relates to a leak detection composition and method for use with air conditioning and other refrigeration systems.

BACKGROUND ART

Daylight visible dyes have been employed to detect leaks in refrigeration systems utilizing fluorocarbon refrigerants and refrigeration oils. At the site of the leak, the escaping refrigerants and refrigeration oils containing visible dyes are detectable in normal light to a slight extent depending on the size of the leak.

Traditionally, oil soluble azo and anthraquinone dyes have been used as leak detectors in fluorocarbon refrigerants. These dyes are insufficiently stable at high temperatures such as those produced in automotive and commercial refrigeration systems. Low solubility of these dyes in the refrigerants and refrigeration oils results in clumps of dye powders being circulated through the system. Such clumps may clog the refrigeration system.

U.S. Patent 1,915,965 discloses a method of testing for leaks in a refrigeration system of the compression type. Basic daylight visible dyes, such as methyl violet base, crystal violet, auramine B, rhodamine B, etc., are disclosed for use as leak detectors in

refrigeration systems. These basic dyes are unstable at high temperatures and may be converted to tars which plug the system. Such basic dyes also have a low solubility in widely used refrigeration oils.

U.S. Patent 4,369,120 discloses anthraquinone blue dyes for use as visual leak detectors in refrigerants, refrigeration oils and admixtures of both. These blue dyes are visual leak indicators which readily stain surrounding areas of a leak in a refrigeration system due to their intense blue color which is differentiable from leaks of other fluid systems; e.g., red fuel oil or other colored fluids in automotive systems. The problems with these blue dyes are inherent to all visible dyes as described above.

SUMMARY OF THE INVENTION

The present invention provides an improved leak detectable refrigeration composition that fluoresces under ultraviolet light, which comprises an effective amount of a fluorescent alkyl-substituted perylene dye dissolved in a refrigeration liquid comprising a polyhalogenated hydrocarbon refrigerant and a refrigeration oil.

The polyhalogenated hydrocarbon refrigerant may be selected from the group consisting of

trichloromonofluoromethane,

dichlorodifluoromethane,

monochlorotrifluoromethane,

dichloromonofluoroethane,

monochlorodifuluoromethane,

trichlorotrifluoroethane,

dichlorotetrafluoroethane,

1,1,2-trichloro-1,2,2-trifluoroethane,

1,2-dichloro-1,1,2,2-tetrafluoroethane,
1,1-difluoroethane/dichlorodifluoromethane azeotrope,
chloropentafluoroethane/chlorodifluoromethane azeotrope,
chlorotrifluoromethane/trifluoromethane azeotrope,
bromotrifluoromethane,
trifluoromethane,
chloropentafluoroethane,
difluoromethane/chloropentafluoroethane azeotrope,
chloropentafluoroethane/1,1-difluoroethane azeotrope,
dichlorodifluoromethane/chlorofluoromethane azeotrope,
chlorofluoromethane/1,2-dichlorotetrafluoroethane azeotrope,
difluoromethane,
1,2-dibromotetrafluoroethane,
1,1,1-trifluoroethane,
1,1-difluoro-1-chloroethane,
1,1-difluoroethane,
bromotrifluoromethane/difluoromethane azeotrope,
1,2-dichlorotetrafluoroethane/dichlorofluoromethane azeotrope, and
hexafluoroethane/trifluoromethane azeotrope.

The refrigeration oil may be selected from the group consisting of paraffinic oils and alkylated benzenes.

The fluorescent dye is an alkyl-substituted perylene dye that is soluble in the refrigeration liquid and does not adversely affect the operation of a refrigeration system.

Fluorescent dyes are preferable to conventional visible dyes because exposure thereof to ultraviolet light provides fluorescence that is more readily apparent. It is also easier to differentiate fluorescent dyes from other standard daylight visible dyes used in automotive fluid systems such as engine oil fluid, transmission fluid, and coolant fluid. Fluorescent dyes are also advantageous as they are barely visible in daylight, even though readily visible under ultraviolet light. Furthermore, fluorescent dyes are non-staining because they are easily washable with aliphatic non-toxic solvents, as opposed to the toxic aromatic or chlorinated solvents required to clean visible dyes.

In accordance with the preferred composition, this invention utilizes a fluorescent dye which is stable at high temperatures up to 400° Fahrenheit, possesses sufficiently high solubility in a number of currently used refrigeration liquids, does not change the properties of refrigeration oils into which it is dissolved, does not produce adverse effects on refrigeration system parts such as gaskets,

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compressors and the like, and may be easily differentiated from other fluid systems leak indicators. The composition of the present invention will not stain acrylic finishes, such as automotive paint, or refrigerator cabinets, as well as the skin and clothing of system operators.

There is no need to change fluids after the leak has been reparied, because the dye can coexist with system fluids without adversely affecting the refrigeration system parts. As the dye is not removed from the system, the test may be repeated to insure that the leak has been successfully repaired and that no additional leaks exist. After the leak is repaired, excess oil and dye may be removed from surface areas with any aliphatic non-toxic solvent, not requiring toxic, aromatic or chlorinated solvents.

Further, according to the invention, a method for detecting leakage in a refrigeration system comprises circulating a composition as described above through the refrigeration system and thereafter subjecting the refrigeration system to an ultraviolet light to fluoresce any dye which escapes therefrom through a leak to thereby locate the leak such that the leak can be repaired. If the leak is sufficiently large, streams of fluorescently dyed refrigerant may be seen emanating from the leak source. Traditional daylight visible dyes are not sufficiently soluble in the refrigerant to act likewise.

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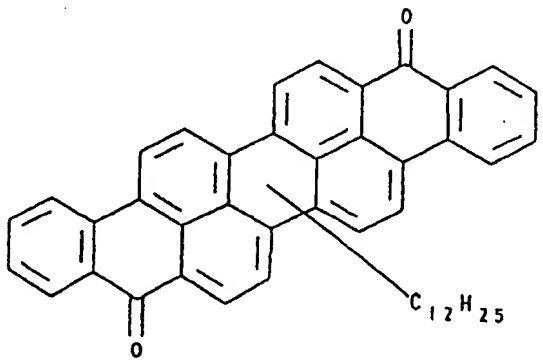
DESCRIPTION OF THE INVENTION

The present invention is directed to a composition useful in the detection of leaks in refrigeration systems. The composition includes a refrigeration liquid, comprising a polyhalogenated hydrocarbon refrigerant and a refrigeration oil and an effective amount (for example at least about 0.001 grams based on 100 grams of the refrigeration liquid up to about the solubility limit) of the fluorescent dye dissolved therein. The fluorescent dye is a fluorescent alkyl-substituted perylene that is soluble in the refrigeration liquid. Preferably, the fluorescent dye has the structure:

Dinaptho(1,2,3-cd: 1',2',3'-lm)perylene - 9,18-dione dodecyl derivative of the formula:



which is commercially available as Fluorescent Yellow 131 SC from Morton Chemical Company.

Polyhalogenated hydrocarbon refrigerants which may be used include:

trichloromonofluoromethane,

dichlorodifluoromethane,

monochlorotrifluoromethane,

dichloromonofluoroethane,

monochlorodifluoromethane,

trichlorotrifluoroethane,

dichlorotetrafluoroethane,

1,1,2-trichloro-1,2,2-trifluoroethane,

1,2-dichloro-1,1,2,2-tetrafluoroethane,

1,1-difluoroethane/dichlorodifluoromethane azeotrope,

chloropentafluoroethane/chlorodifluoromethane azeotrope,

chlorotrifluoromethane/trifluoromethane azeotrope,

bromotrifluoromethane,
trifluoromethane,
chloropentafluoroethane,
difluoromethane/chloropentafluoroethane azeotrope,
chloropentafluoroethane/1,1-difluoroethane azeotrope,
dichlorodifluoromethane/chlorofluoromethane azeotrope,
chlorofluoromethane/1,2-dichlorotetrafluoroethane azeotrope,
difluoromethane,
1,2-dibromotetrafluoroethane,
1,1,1-trifluoroethane,
1,1-difluoro-1-chloroethane,
1,1-difluoroethane,
bromotrifluoromethane/difluoromethane azeotrope,
1,2-dichlorotetrafluoroethane/dichlorofluoromethane azeotrope, and
hexafluoroethane/trifluoromethane azeotrope.

The refrigeration oils which may be used include paraffinic oils and alkylated benzenes. In the refrigeration liquid mixture of the polyhalogenated hydrocarbon refrigerant and the refrigeration oil, the ratio of the refrigeration oil to the refrigerant may be in the range from about 1:3 to about 1:100.

A method according to this invention for detecting leakage in a refrigeration system is performed by adding a fluorescent dye solution or fluorescent dye to refrigeration oil and thereafter introducing the oil with the dye therein into a polyhalogenated hydrocarbon refrigerant of a refrigeration system.

Another method according to this invention is performed by adding a fluorescent dye or fluorescent dye solution into a polyhalogenated hydrocarbon refrigerant and thereafter introducing the refrigerant into the refrigeration system.

In performing both methods, the refrigeration system is operated for a period of time to thoroughly mix the fluorescent dye within the refrigeration system fluid. The system is then subjected to an ultraviolet light to fluoresce any dye which escapes therefrom through a leak. Visual inspection under the ultraviolet light will locate the leak. After the leak is repaired, excess fluid and dye may be removed from the surface area with a solvent. The refrigeration system is then operated again to insure that the leak has been successfully repaired, and that no additional leaks exist.

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A further method for detecting the leakage in a refrigeration system includes circulating through the refrigeration system the refrigeration composition as described above including a mixture of the refrigerant and the refrigeration oil having the fluorescent dye dissolved therein in a sufficient amount such as at least 0.001 grams per 100 grams of the refrigeration liquid and subjecting the system to an ultraviolet light to locate the leakage. After detection, the leaking portion may be repaired.

Another method for detecting the leakage in a refrigeration system can be performed by dissolving the fluorescent dye in the refrigeration oil, then introducing the dye and oil into the polyhalogenated hydrocarbon refrigerant, and then introducing the refrigerant with dye and oil therein into a refrigeration system. After a certain period of operation, various portions of the refrigeration system are subjected to an ultraviolet light source to fluoresce any dye which escapes therefrom through a leak to thereby locate the leak such that the leak can be repaired.

The present invention may be worked in a manner similar to the following examples.

EXAMPLE 1

About 0.5 ounces of a napthenic oil solution containing 10% Naphtho [3,2,1-kl] xanthene 2,8 dimethyl fluorescent dye was added to a 14 ounce high pressure metal can. Fourteen ounces of dichlorodifluoromethane was added to the can and the can was sealed. The contents of the can were added to an automotive air conditioning system using a charging hose having a safety valve.

Sufficient dichlorodifluoromethane was then added to fill the air conditioning system, and the system was run for five minutes to insure mixing of the fluorescent dye with the refrigeration fluid. An ultraviolet light was used to scan the air conditioning system to check for leaks. Bright yellowish green fluorescence was observed at a fluid line junction indicating a leak which was thereafter repaired. The leak site was cleaned with an aliphatic cleaning solvent before the system was started again and allowed to run for five minutes. Once again, the air conditioning system was scanned with an ultraviolet light, looking for more leaks. As no fluorescence was observed, the leak of the air conditioning system has been successfully repaired.

EXAMPLE 2

A high pressure metal can similar to the one described in Example 1 was filled with 0.25 ounces of naphthenic oil solution having 25% 4, butyl amino - n butyl naphthalimide fluorescent dye therein and fourteen ounces of dichlorodifluoromethane. The contents of the can were introduced into an automotive air conditioning system of a brand new automobile in an automotive assembly plant. A recommended amount of dichlorodifluoromethane was added to the automotive air conditioning system, and allowed to run for five minutes. Ultraviolet light was

used to scan the system, and a bright turquoise greenish fluorescence was observed at the junction of the refrigeration hose and the compressor, indicating a leak. The leak was repaired, and the air conditioning system was checked again as described in Example 1. No more fluorescence was observed, indicating that the leak had been successfully repaired.

While the best modes have been described in detail, those familiar with the art to which this invention relates will recognize various alternative compositions and methods for practicing the invention as defined by the following claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A refrigeration composition that fluoresces under ultraviolet light which comprises:

a. a refrigeration liquid comprising:

i. a polyhalogenated hydrocarbon refrigerant, and

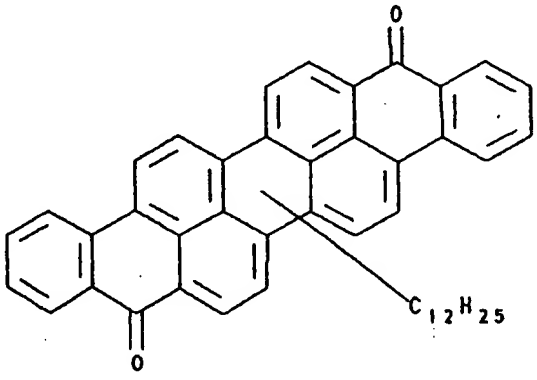
ii. a paraffinic or alkylated benzene refrigeration oil; and

b. an effective amount of a fluorescent alkyl-substituted perylene dye compound;

wherein the fluorescent dye is soluble in the refrigeration liquid and does not adversely affect the operation of a refrigeration system.

2. The composition of claim 1 wherein the refrigeration oil comprises a paraffinic oil.

3. The composition of claim 1 wherein the perylene compound comprises dinaphtho[1, 2, 3-cd: 1', 2', 3'-lm]perylene-9,18-dione dodecyl derivative having the structure:



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4. The composition of claim 1 wherein the refrigeration liquid comprises about 3 to 100 grams of the refrigerant per gram of the refrigeration oil.

5. A refrigeration composition that fluoresces under ultraviolet light which comprises:

a. a refrigeration liquid comprising:

i. a polyhalogenated hydrocarbon refrigerant, and

ii. a paraffinic or alkylated benzene refrigeration oil; and

b. an effective fluorescent amount of a fluorescent alkyl-substituted perylene dye compound;

wherein the concentration of the fluorescent dye is from about 0.001 wt. % up to about the solubility limit of the fluorescent dye in the refrigeration liquid, the fluorescent dye is soluble in the refrigeration liquid and does not adversely affect the operation of a refrigeration system.

6. The composition of claim 5 wherein the refrigeration oil comprises a paraffinic oil.

7. The composition of claim 5 wherein the perylene compound comprises dinaphtho[1, 2, 3-cd: 1', 2', 3'-lm]perylene-9,18-dione dodecyl derivative having the structure:

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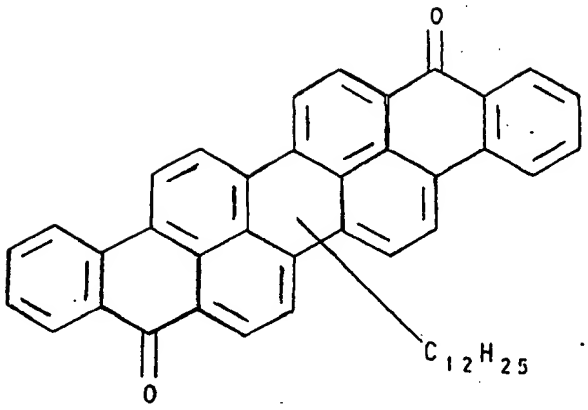

8. The composition of claim 5, wherein the refrigeration liquid comprises about 3 to 100 grams of refrigerant per gram of refrigeration oil.

9. The composition of claim 5, wherein the refrigeration liquid comprises dichlorodifluoromethane.

10. A method for detecting leakage in a refrigeration system, which method comprises:

a. dissolving a fluorescent alkyl-substituted perylene dye compound into a paraffinic or alkylated benzene refrigeration oil;

b. introducing the refrigeration oil with the dye dissolved therein into a refrigeration system containing a polyhalogenated hydrocarbon refrigerant to form a leak detection composition comprising the dissolved fluorescent alkyl-substituted perylene dye compound, the refrigeration oil and the polyhalogenated hydrocarbon refrigerant, wherein the fluorescent alkyl-substituted perylene dye compound does not adversely affect the operation of

the refrigeration system; and

c. subjecting the refrigeration system to an ultraviolet light to fluoresce any leak detection composition which escapes therefrom through a leak whereby the leak is located.

11. A method for detecting leakage in a refrigeration system, which method comprises:

a. dissolving a fluorescent alkyl-substituted perylene dye compound in a paraffinic or alkylated benzene refrigeration oil;

b. introducing the refrigeration oil with the dye dissolved therein into a polyhalogenated hydrocarbon refrigerant to form a leak detection composition comprising the dissolved fluorescent alkyl-substituted perylene dye compound, the refrigeration oil and the polyhalogenated hydrocarbon refrigerant, wherein the fluorescent alkyl-substituted perylene dye compound does not adversely affect the operation of a refrigeration system;

c. introducing the leak detection composition into a refrigeration system; and

d. subjecting the refrigeration system to an ultraviolet light to fluoresce any leak detection composition which escapes therefrom through the leak whereby the leak is located.

12. A method for detecting leakage in a refrigeration system, the method comprising:

a. circulating through the refrigeration system a composition comprising:

i. a refrigeration liquid comprising:

(1) a polyhalogenated hydrocarbon refrigerant, and

(2) a paraffinic or alkylated benzene refrigeration oil; and

ii. an effective amount of a fluorescent alkyl-substituted perylene dye compound;

b. subjecting the refrigeration system to an ultraviolet light to fluoresce the fluorescent dye which escapes therefrom through a leak whereby the leak is located;

wherein the fluorescent dye is soluble in the refrigeration liquid and does not adversely affect the operation of a refrigeration system.

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PATENT AGENTS